

Sequentially Evaporated Thin Y-Ba-Co-O Superconducting Films on Microwave Substrates

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SEQUENTIALLY EVAPORATED THIN Y-Ba-Cu-O SUPERCONDUCTING FILMS ON MICROWAVE SUBSTRATES

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ABSTRACT

The development of high T_c superconducting thin films on various microwave substrates is of major interest to evaluate their applications in space electronic systems. Thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been formed on SrTiO_3 , MgO , ZrO_2 coated Al_2O_3 and LaAlO_3 substrates by multi-layer sequential evaporation and subsequent annealing in oxygen. The technique allows controlled deposition of Cu, BaF_2 and Y layers, as well as the ZrO buffer layers, to achieve reproducibility for microwave circuit fabrication. The three layer structure of $\text{Cu}/\text{BaF}_2/\text{Y}$ is repeated a minimum of four times. The films have been annealed in an ambient of oxygen bubbled through water at temperatures between 850°C and 900°C followed by slow cooling ($-2^\circ\text{C}/\text{minute}$) to 450°C , a low temperature anneal, and slow cooling to room temperature. Annealing times have ranged from 15 minutes to 5 hrs at high temperature and 0 to 6 hr at 450°C . Silver contacts for four probe electrical measurements have been formed by evaporation followed with an anneal at 500°C . The films have been characterized by resistance-temperature measurements, energy dispersive x-ray spectroscopy, x-ray diffraction and scanning electron microscopy. Critical transition temperatures have ranged from 30 K to 87 K as a function of the substrate, composition of the film, thicknesses of the layers and annealing conditions. Microwave ring resonator circuits are also patterned on these MgO and LaAlO_3 substrates.

1.0 INTRODUCTION

The development of thin films of the high critical temperature (T_c) superconducting oxides on various microwave substrates is of major interest as it allows evaluation of the superconductors for application in space electronic systems. A large amount of work has been reported on these films on substrates such as strontium titanate (SrTiO_3) and yttrium stabilized zirconia (YSZ), however these substrates are not suitable for microwave applications due to large dielectric constants or microwave losses. Substrates which are more suitable for microwave applications include magnesium oxide (MgO), sapphire, alumina (Al_2O_3) and lanthanum aluminate (LaAlO_3). These substrates have dielectric constants of approximately 10, 9.4 or 11.6, 9.8 and 15.3¹ respectively, although the dielectric constant of LaAlO_3 may be somewhat higher². LaAlO_3 substrates are of particular interest since they have a comparable crystal structure to SrTiO_3 but significantly better microwave properties.

¹ R. W. Simon, C. E. Platt, A. E. Lee, G. S. Lee, K. P. Daly, M. S. Wire, J. A. Levine and M. Urbanik, "Low-loss Substrate for Epitaxial Growth of High-Temperature Superconductor Thin Films," *Appl. Phys. Lett.*, 53(26), 2677 (1988).

² F. A. Miranda, N. L. Gordon, V. O. Heinen, B. T. Ebiyara and K. B. Bhasin, "Measurement of Complex Permittivity of Microwave Substrates in the 20 to 300 K Temperature Range From 26.5 to 40.0 GHz," Accepted for presentation at the Cryogenic Engineering Conference, July 24-28, 1989, Los Angeles, CA.

A large variety of techniques have been used to form high temperature superconducting thin films. One such technique consists of the sequential evaporation of a multi-layer stack containing the constituents of the superconductor followed by annealing in an oxygen ambient^{3,4,5,6,7,8}. When performed by electron beam evaporation from a multi-hearth gun, this technique allows deposition of films with little spatial variation of stoichiometry across the substrate as all components of the film are evaporated from the same point in space. The stoichiometry of the films is also easily adjusted by controlling the thickness of the individually deposited layers. This technique has been employed with a variety of starting materials; Y, Ba and Cu metals themselves, oxides and BaF₂.

We have performed sequential evaporation of Cu, Y and BaF₂ to study the formation of superconducting films on SrTiO₃, MgO, sapphire, alumina and LaAlO₃ substrates. For the sapphire and alumina substrates, we have used a thin film of ZrO₂ as a buffer layer. We have varied the stoichiometry of the films by adjusting the thicknesses of the individual layers. Films of fixed composition have also been differently annealed to assess the influence of annealing conditions. The resistivity of the films has been measured with a standard four point probe technique between the temperatures of 10 K and 300 K.

2.0 EXPERIMENTAL PROCEDURE

Deposition of the films was performed in a CHA Industries electron beam evaporator. The system is equipped with a four hearth gun, allowing deposition of the multi-layer stack without breaking vacuum. Thickness of the layers was controlled via an Inficon XTC thickness monitor and rate controller. The depositions were calibrated by measurements of step heights using a surface profilometer. The ZrO₂ buffer layers for the sapphire and alumina substrates were also deposited in this evaporator.

A cross sectional drawing of the structure of a typical as deposited film is shown in Figure 1. Copper was deposited on the substrate first. This was followed by a layer of yttrium which was followed by barium fluoride. For most of our depositions, this multi-layered sequence was repeated four times for a total of twelve layers. For substrates on which a buffer layer was employed, the ZrO₂ layer was deposited prior to deposition of the first copper layer. The thicknesses of the individual layers are varied to alter the composition of the film. We reference the composition of the films through the barium/yttrium and copper/yttrium atomic ratios. We have investigated the properties of films with barium/yttrium ratios ranging from 1.9 to 4.0 and copper/yttrium ratios ranging from 2.8 to 3.5. We have used barium fluoride rather than elemental barium since barium fluoride is less reactive.

The deposited films were annealed in a hot wall, programable, quartz tube furnace. The furnace was purged with oxygen prior to inserting the samples. In some cases, the furnace was heated to the annealing temperature prior to insertion of the samples. The samples were pushed into the preheated furnace using a fast push of approximately 30 sec duration or a slow push with a 5 minute duration. Otherwise the samples were pushed into the center of the cool furnace and the

³ A. Mogro-Campero and L. G. Turner, "Thin Films of Y-Ba-Cu-O on Silicon and Silicon Dioxide," Appl. Phys. Lett., 52, 1185 (1988).

⁴ C. X. Qiu and I. Shih, "Y-Ba-Cu-O Thin Films Prepared by a Multi-Layer Vacuum Method," Appl. Phys. Lett., 52, 587 (1988).

⁵ C-A. Chang, C. C. Tsuei, C. C. Chi and T. R. McGuire, "Thin Film YBaCuO Superconductors Formed by Cu/BaO/Y₂O₃ Layer Structures, Appl. Phys. Lett. 52, 72 (1988).

⁶ Z. L. Bao, F. R. Wang, Q. D. Jiang, S. Z. Wang, Z. Y. Ye, K. Wu, C. Y. Li, and D. L. Yin, "YBaCuO Superconducting Thin Films With Zero Resistance at 84 K by Multilayer Deposition," Appl. Phys. Lett. 51, 946 (1987).

⁷ N. Hess, L. R. Tessler, U. Dai and G. Deutscher, "Preparation and Patterning of YBaCuO Thin Films Obtained by Sequential Deposition of CuO_x/Y₂O₃/BaF₂, Appl. Phys. Lett. 53, 698 (1988).

⁸ G. J. Valco, N. J. Rohrer, J. D. Warner and K. B. Bhasin, "Sequentially Evaporated Thin Y-Ba-Cu-O Superconductor Films: Composition and Processing Effects," American Institute of Physics Conference Proceedings, to be published.

temperature was ramped to the annealing temperature at rates from 20 °C/minute to 80 °C/minute. Annealing temperatures ranged from 850 °C to 900 °C. The duration of the anneals ranged from 15 minutes to 3 hr. The temperature was then ramped to 450 °C at a rate of -2 °C/minute. The samples were held at 450 °C for 6 hr and then the temperature was ramped to room temperature at -2 °C/minute. During the high temperature portion of the anneal the ambient consisted of ultra high purity oxygen bubbled through room temperature water to assist in removal of fluorine from the films. Dry oxygen was used during all other portions of the annealing process.

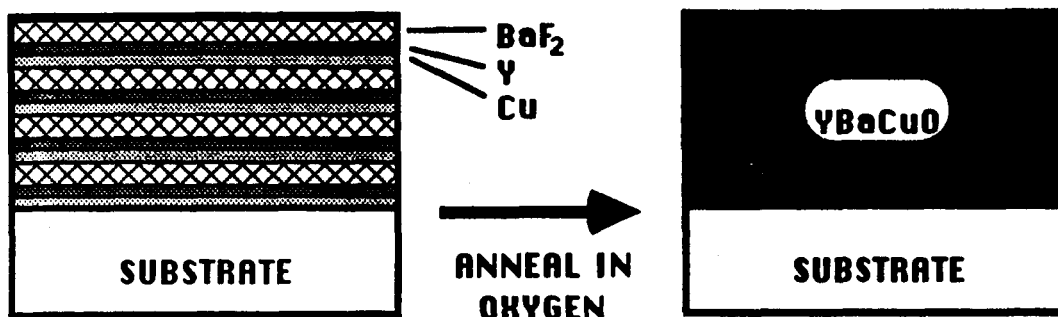


Figure 1: Schematic representation of the as deposited multi-layer structure of the film on the left and the superconducting film after annealing on the right.

Ohmic contacts were formed on the films to allow measurement of the resistance as a function of temperature. Most of the samples were rectangular in shape with widths of approximately 5 mm and lengths of approximately 1 cm. The contacts for these samples were deposited by evaporation of 1 μ m of silver through shadow masks to produce four stripes across the width of the samples. The contacts were annealed in dry oxygen at 500 °C for 1 hr. They were placed in the tube furnace at room temperature and the temperature was ramped up at 20 °C/minute. At the end of the anneal the temperature was ramped to 250 °C at a rate of -2 °C/minute and then to room temperature at -1 °C/minute.

To allow measurement of the resistance of the films as a function of temperature, the samples were cooled in a closed cycle helium refrigerator. They were mounted onto a sample holder and gold ribbon bonds were made between the silver contacts and bonding posts. A four probe DC measurement was employed to determine the resistance as the sample temperature was lowered. A few samples were measured both while cooling or while heating, with the same results in both directions. The criteria for determination of T_c was the resistivity decreasing to the noise level of approximately 10^{-9} Ω -cm. Measurements were continued to well below the transition temperature for superconducting films or to approximately 10 K for non-superconducting films.

Scanning electron microscopy (SEM) was employed to observe the morphology of several of the films. In addition, some films on SrTiO₃ substrates were analyzed by x-ray diffraction spectroscopy (XDS) to check orientation and the presence of other phases. Auger electron spectroscopy (AES) was employed to study the film/buffer/substrate interfaces of several samples with ZrO₂ buffer layers.

3.0 RESULTS

The annealing cycle and composition of the film have a major influence on the properties of the resulting film. Figure 2 shows the normalized resistance as a function of temperature for four samples deposited at the same time onto SrTiO₃ but annealed with different procedures. The composition of the as deposited films was Cu/Y=3.11 and Ba/Y=2.20. They were annealed for 45 minutes at either 850 °C, 875 °C or 900 °C and with either a fast push (30 sec) or a slow push (5 minutes) into the center zone of the furnace. There is a marked improvement in the critical temperature, transition width and normal state resistance characteristic of the films as the annealing temperature was increased from 850 °C to 900 °C. The difference between the two samples annealed at 850 °C with different push rates demonstrates the influence of the heating rate during the anneal. The film annealed at 900 °C and given the slow push was the best.

Figure 3 shows the effect of heating rate for films with the optimal as deposited composition ($\text{Cu}/\text{Y}=3.00$, $\text{Ba}/\text{Y}=2.25$) on SrTiO_3 . All of these films were annealed for 45 minutes at 900°C with heating rates of either a slow push (5 minutes), $50^\circ\text{C}/\text{minute}$ ramp or $20^\circ\text{C}/\text{minute}$ ramp. The intermediate heating rate, $50^\circ\text{C}/\text{minute}$, resulted in the film with the sharpest resistive transition and a critical temperature of 85 K.

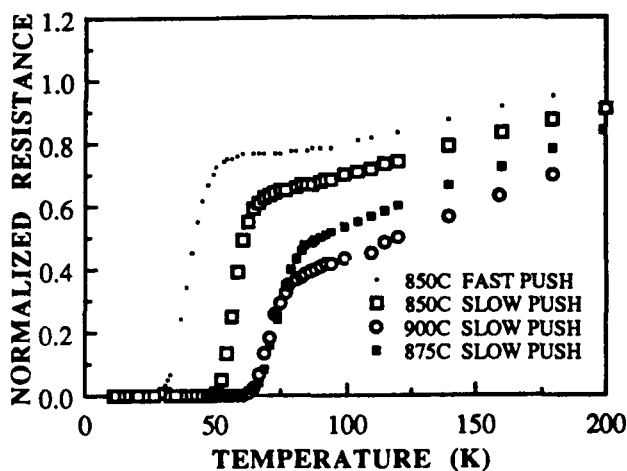


Figure 2: Resistance normalized to 300 K as a function of temperature for four samples on SrTiO_3 substrates with different annealing cycles. $\text{Cu}/\text{Y}=3.11$, $\text{Ba}/\text{Y}=2.20$. Annealed 45 minutes.

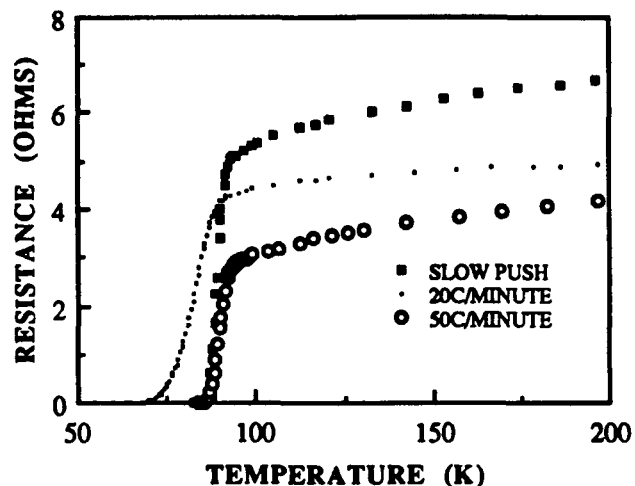


Figure 3: Resistance as a function of temperature for three samples on SrTiO_3 substrates with different annealing cycles. $\text{Cu}/\text{Y}=3.00$, $\text{Ba}/\text{Y}=2.25$. Annealed 45 minutes at 900°C .

Figure 4 shows the distribution of transition temperature for films with various ratios of Cu/Y and Ba/Y . Each film was made with a 12 layer deposition and had a thickness between 1.0 and $1.2\ \mu\text{m}$ before annealing. All of the samples were annealed for 45 minutes at 900°C using a slow push. A detailed discussion of the variation of the resistive transition with composition is given in a previous paper by the authors⁸. Those films deposited with a Ba/Y ratio of greater than approximately 2.2 have a metallic normal state resistance-temperature characteristic. This was also true of two films with larger Ba/Y ratios (3.0 and 4.0) which did not completely achieve zero resistance although they had a sharp onset and narrow transition width.

The morphology of the films is dependent on the initial rate of heating during the anneal. For the films of Figure 3, discussed above, the film with the $50^\circ\text{C}/\text{minute}$ heating rate has a dense "basketweave" morphology. SEM micrographs typical of this morphology were presented in an earlier paper by the authors⁹. X-ray diffraction spectroscopy showed that this film has primarily the a-axis oriented perpendicular to the substrate but does show some c-axis orientation. The basketweave morphology was also present

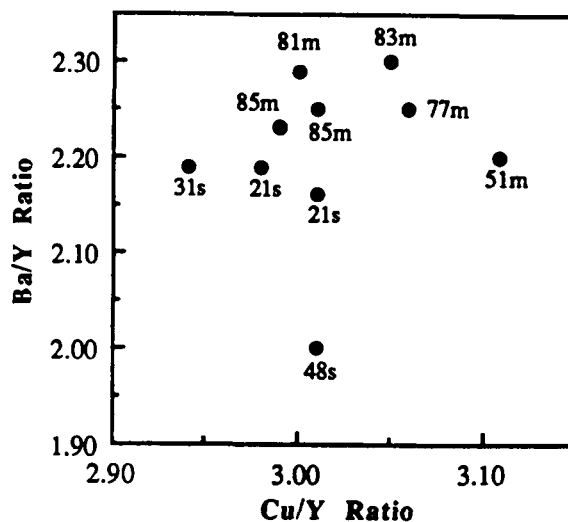


Figure 4: Distribution of T_c for films of various composition on SrTiO_3 annealed at 950°C for 45 minutes with a slow push. The number with each point indicates the critical temperature while the letter indicates the behavior in the normal state: metallic or semiconducting.

⁹ G. J. Valco, N. J. Rohrer, J. J. Pouch, J. D. Warner, K. B. Bhasin, "Characterization of ZrO_2 Buffer Layers for Sequentially Evaporated Y-Ba-Cu-O On Si and Al_2O_3 Substrates," Proceedings of the Conference on the Technology of Thin Film Superconductors, submitted for publication.

in the film annealed with the 5 minute push, although it was not as dense. The film on the sample heated at a rate of 20 °C/minute did not exhibit the basketweave structure, but had shorter, randomly oriented grains that appeared to lie parallel to the surface of the substrate. The critical current density was an order of magnitude larger for the sample with the 50 °C/minute heating rate than for the film heated at 20 °C/min. The presence of the oriented basketweave morphology is also enhanced with thinner films⁹.

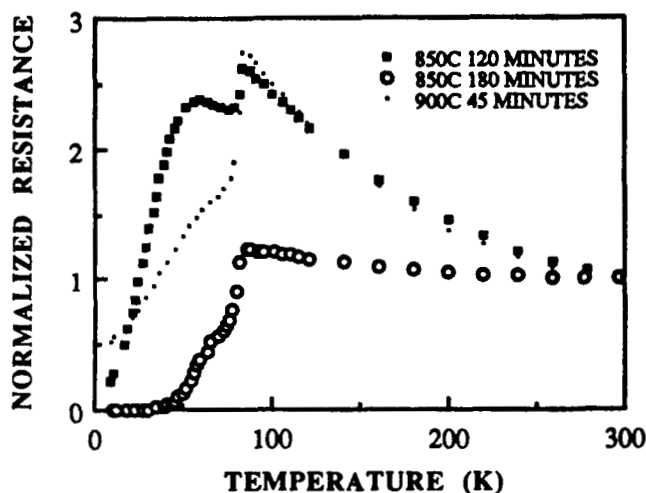


Figure 5: Resistance normalized to 300K as a function of temperature for three samples on MgO substrates with different annealing cycles. Cu/Y=3.02, Ba/Y=2.26.

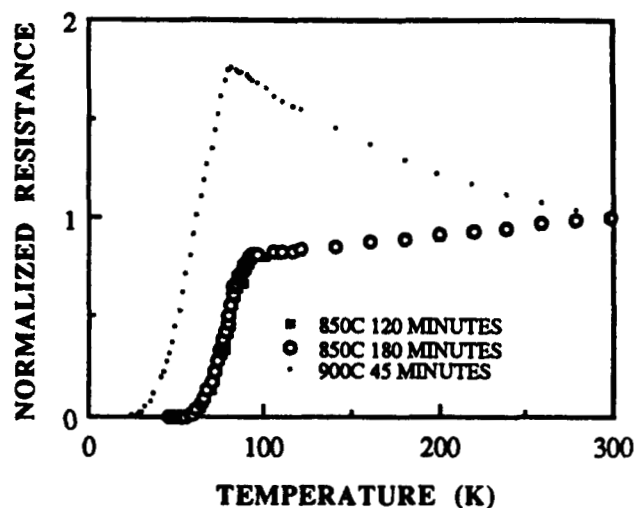


Figure 6: Resistance normalized to 300K as a function of temperature for three samples on MgO substrates with different annealing cycles. Cu/Y=3.01, Ba/Y=2.00.

In contrast with the films on SrTiO₃ substrates, films on MgO require lower annealing temperatures but longer durations. Figures 5 and 6 show the normalized resistance-temperature characteristics for films of two different composition on MgO substrates which were annealed under different conditions. The samples indicated by the squares have been annealed at 900 °C for 45 minutes in a procedure identical to that used for SrTiO₃. The samples indicated by the crosses and circles had been annealed at 850 °C for 120 and 180 minutes respectively. In Figure 5, the films had an as deposited composition of Cu/Y=3.02 and Ba/Y=2.26, which is near the optimum composition used on SrTiO₃ substrates. Although none of the samples became superconducting, they all showed an onset of superconductivity and there is a clear improvement for the lower temperature, long duration anneal. The data presented in Figure 6 are for samples with an as deposited composition of Cu/Y=3.01 and Ba/Y=2.00. The sample annealed at 900 °C had a semiconducting behavior in the normal state, a very broad transition with a long tail, and never achieved zero resistance while the samples annealed at 850 °C displayed a metallic behavior in the normal state and achieved zero resistance at approximately 51 K.

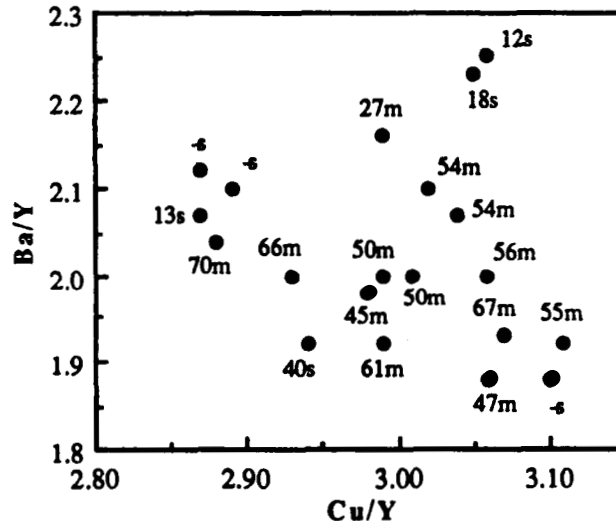


Figure 7: Distribution of T_c for films of various composition on MgO annealed at 850 °C for 3 hr. The number with each point indicates T_c while the letter indicates the behavior in the normal state : metallic or semiconducting.

Figure 7 shows the distribution of T_c for several films on MgO as a function of Cu/Y and Ba/Y ratio. All of these samples were annealed at 850 °C for 3 hrs with a slow push into the furnace. It is apparent that the as deposited composition to produce good films on MgO is different than for SrTiO₃, with the major difference being a lower Ba/Y ratio. Films with compositions toward the center of the plot have metallic normal state behavior, while those with extreme compositions exhibit a semiconducting behavior. Many of these films have broad resistive transitions with a shoulder as in Figure 5 and long low resistance tails. The film with the best T_c had an as deposited composition of Cu/Y=2.88 and Ba/Y=2.04, and its resistance-temperature characteristic is shown in Figure 8.

ZrO₂ buffer layers were used for films on Si, sapphire and Al₂O₃ substrates as described above. Detailed Auger analysis of the performance of the buffer layers on silicon and sapphire substrates has been previously reported⁹. The key features of the performance of these buffer layers determined by the Auger analysis was that ZrO₂ appears to form a stable buffer layer for YBa₂Cu₃O_{7- δ} films on sapphire. In contrast with the films on silicon, the films on sapphire with 0.2 μ m buffer layers exhibited zero resistance for a variety of compositions and there was an improvement in the resistive transition with increased annealing duration similar to that observed for MgO substrates. Superconducting films were achieved on silicon when thicker 0.5 μ m and 0.9 μ m buffer layers were deposited.

We have extended the use of ZrO₂ buffer layers to form superconducting YBa₂Cu₃O_{7- δ} films on Al₂O₃ substrates. The resistance-temperature characteristic of a film with an as deposited composition of Cu/Y=3.10 and Ba/Y=1.88 is shown in Figure 9. The sample was annealed for 180 minutes at 850 °C. It had a metallic normal state characteristic and reasonably sharp transition. Its critical temperature was 72 K due to a low resistance tail on the transition. The distribution of critical temperature for films of several compositions on alumina substrates is shown in Figure 10. The dependence of the properties of these films on composition more closely resembles that of films on MgO than on SrTiO₃.

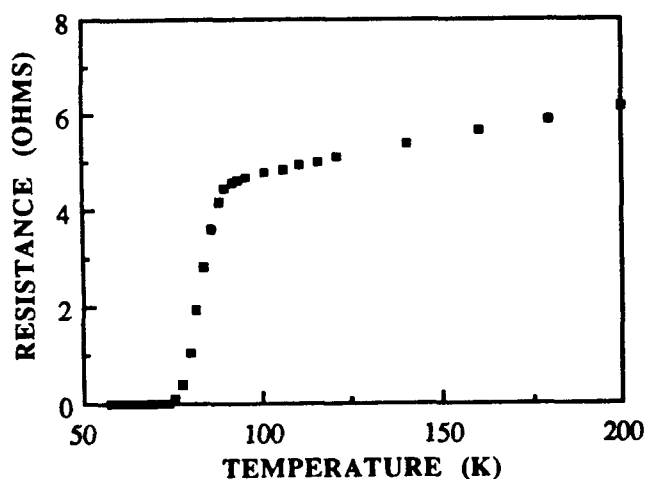


Figure 9: Resistance as a function of temperature for a film on alumina with a ZrO₂ buffer layer. Cu/Y=3.10, Ba/Y=1.88. Annealed 3 hr at 850 °C.

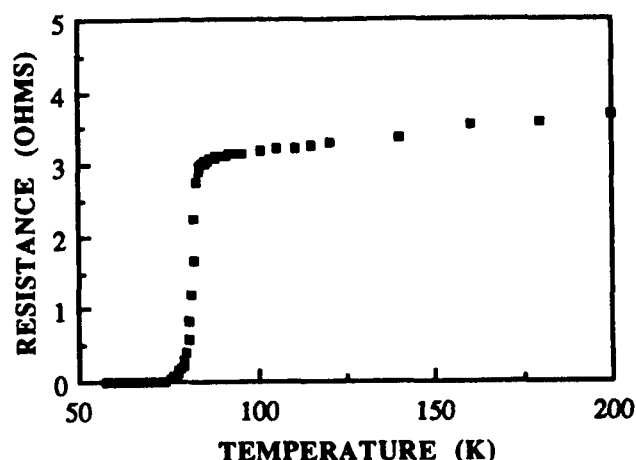


Figure 8: Resistance as a function of temperature for a film on MgO. Cu/Y=2.88, Ba/Y=2.04. Annealed at 850 °C for 3 hr.

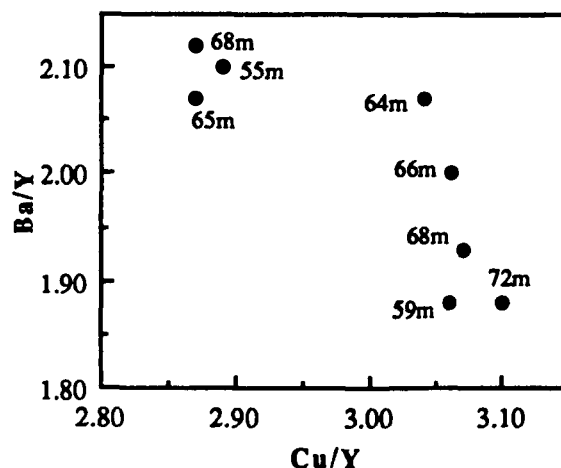


Figure 10: Distribution of T_c for films of various composition on alumina with a ZrO₂ buffer. Annealed at 850 °C for 3 hr. The number with each point is T_c while the letter shows the normal state behavior: metallic or semiconducting.

Figure 11 shows the normalized resistance as a function of temperature for three films formed on LaAlO_3 . The films were deposited at the same time with a composition of $\text{Cu}/\text{Y}=3.00$ and $\text{Ba}/\text{Y}=2.25$ and a twelve layer sequence, but a total thickness of only $0.5\ \mu\text{m}$ before annealing. The films was annealed at $950\ ^\circ\text{C}$ for 45 minutes with heating rates of $50\ ^\circ\text{C}/\text{minute}$ or $100\ ^\circ\text{C}/\text{minute}$ or a slow push. All of the films had a metallic characteristic above the transition temperature. The film which received the slow push into the furnace had the highest critical temperature, approximately 80 K.

Microstrip ring resonators have been designed for measurement at 30 GHz on LaAlO_3 and MgO substrates. Films on these substrates are being patterned into ring resonators via lift-off lithography.

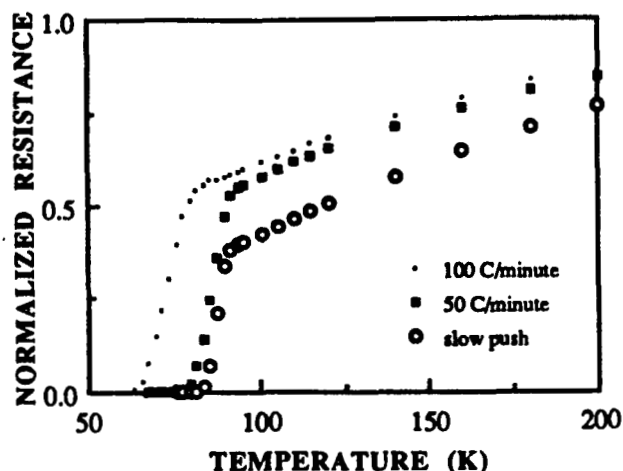


Figure 11: Normalized resistance as a function of temperature for three films LaAlO_3 with different annealing procedures. $\text{Cu}/\text{Y}=3.00$, $\text{Ba}/\text{Y}=2.25$. Annealed 45 minutes at $900\ ^\circ\text{C}$.

4.0 SUMMARY AND CONCLUSIONS

We have employed multi-layer sequential electron beam evaporation to form superconducting films on several different substrates. The best films have been formed of SrTiO_3 where we have achieved a critical temperature of 87 K. Superconducting films have also been achieved on MgO , sapphire, alumina and recently on LaAlO_3 substrates for which a critical temperature of 80 K was obtained. The superconducting films on LaAlO_3 and MgO are being used in the fabrication of microstrip ring resonators to allow testing of the microwave properties of the films at 30 GHz.

5.0 ACKNOWLEDGEMENTS

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